## Assessment of Butte Meconium Data

- The initial CCV (10 ppb Calibration Check) was out of specs for Al, Cu, and Zn. The instrument should have been recalibrated before continuing with the analysis. The initial CCV must be within 10% of the true value before continuing with the run.
- USGS T-231 was evidently used as a second source reference check but was not carried through the digestion process. The values for the reference check are within acceptable limits for about half of the elements, which should fall within 10% of the true value. Two of the elements, Al and Sr, are well over the high calibrator of 10 ppb, resulting in erroneous results.
- It was indicated that a digestion blank, designated as "MBLANK" which was run #36, is the blank that was carried through the digestion process. The Blank (labeled Blank, not "MBLANK") was analyzed before the sample labeled Dorm-4, which was evidently not a meconium sample but possibly a sample collected from one of the campus dorms. The results of the blank appear to be within acceptable limits, with no spikes on any of the analytes of interest. The digestion blank was analyzed at the end of the run. A digestion blank should be analyzed immediately after the QC Calibration Verification Standards are analyzed and before the samples are analyzed. If any of the results of the digestion blank are over the analyte method reporting limits, the source of the problem must be determined before the run continues.
- The LFB and samples were supposedly spiked with 5 ppb As, Cd, and Mn, 20 ppb Cu, and 50 ppb Zn. The spiking solution was analyzed in duplicate at the end of the run. The spreadsheet shows the recovery of the spiked analytes. All three LFBs and both samples that were spiked show 10 ppb across the board for all the elements except for Cu and Zn. Based on the LFB and sample spikes, the Cu spike is probably around 140 ppb, and the Zn spike is probably around 260 ppb. If the spiking solution that was analyzed is the one that was used to spike the LFB and samples, then there should be no recovery for Al, Se, Sr, Mo, Pb, or U. Evidently, a different spiking solution was used other than the one indicated, and/or there may be possible contamination of the samples with Cu and Zn. It was not indicated if the LFB was carried through the digestion process or whether the LFB and samples were spiked before or after they were digested.
- None of the meconium samples exceeded the high calibrator for As or Cd. Almost half of the samples exceeded the high calibrator for Mn, and all samples except Sample ID #1 exceeded the high calibrator for Cu and Zn. Those samples exceeding the high calibrator should have been diluted and rerun, or a linear dynamic range check standard (LDR) should have been analyzed to verify that the reported levels above the high calibrator

**Commented [WL1]:** This is problematic.

**Commented [WL2]:** In a nutshell: Reported spiking solutions don't match the values in the run.

**Commented [WL3]:** This means that the sample may be high, but we can't determine how high because it's off the calibration curve.

were accurate and the detector wasn't saturated, especially for some of the Zn levels. This problem is evident for the Sr values in USGS T-231 that were analyzed. The high calibrator for Sr is 10 ppb. The true value for Sr is 254 ppb; the value indicated on the run data is 753 ppb for the first analysis. The Mn, Cu, and Zn levels are evidently high, but possibly not at the levels indicated since the results were not verified.

- The calibration intensity data was not submitted; therefore the % recovery of the internal standards for the samples could not be assessed. The Quantitative Calibration report was not submitted showing the correlation coefficients for the elemental calibration curves.
- The wash time of 40 seconds between samples seems inadequate, especially for the samples containing over 2 ppm Zn. There could be slight carryover from high to low, but the blank analyzed after Sample ID #15 appears to be in specifications.
- The low standard for most of the elements was 0.10 ppb, which would set the reporting limit at 0.005 ug/g. For Mn and Se, the reporting limit is 0.05 ug/g, and for Al, Cu, and Zn, the reporting limit is 0.5 ug/g. (Based on 1g/50 ml final volume)
- The results for Mn, Cu, and Zn were calculated based on the raw data results and the sample digest weights. (See attached spreadsheet). There was no information submitted showing the results that were reported for comparison.
- If there was any digestate solution left, it would be interesting to analyze the samples on the Optima 3000 ICP for Cu, Mn, and Zinc.
- It would also help to assess the data that was analyzed from the South Carolina Laboratory.

**Commented [WL4]:** DPHHS metals chemist washes for 120 seconds

LW notes:

1. Arsenic: unsure of results because there could be interference with other metals. See PDF with notes from other DPHHS ICP-MS demonstrating interference.
2. Overall summary: We identified issues with several QC methods, therefore we have concerns about the accuracy of the results reported in the manuscript.

**Formatted:** Numbered + Level: 1 + Numbering Style: 1, 2, 3, … + Start at: 1 + Alignment: Left + Aligned at: 0.75" + Indent at: 1"